What is claimed is:

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- 1. A method for electrolytic copper plating on a substrate comprising the steps of providing an electrolytic copper plating solution, and contacting the electrolytic copper plating solution with ozone, wherein the electrolytic copper plating solution comprises a compound comprising the formula of –X-S-Y-, wherein X and Y are independently chosen from hydrogen atom, carbon atom, sulfur atom, nitrogen atom, and oxygen atom, and X and Y may be the same only when they are a carbon atom.
- 2. The method of claim 1, wherein the compound comprising the formula –X-S-Y- is chosen from compounds of formulas (1) to (8)
- (1) $M-SO_3-(CH_2)_a-S-(CH_2)_b-SO_3-M$;
- (2) M-SO₃-(CH₂)_a-O-CH₂-S-CH₂-O-(CH₂)_b-SO₃-M;
- (3) $M-SO_3-(CH_2)_a-S-S-(CH_2)_b-SO_3-M$;
- (4) $M-SO_3-(CH_2)_a-O-CH_2-S-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (5) $M-SO_3-(CH_2)_a-S-C(=S)-S-(CH_2)_b-SO_3-M$;
- (6) $M-SO_3-(CH_2)_a-O-CH_2-S-C(=S)-S-CH_2-O-(CH_2)_b-SO_3-M$;
- (7) A-S- $(CH_2)_a$ -SO₃-M; and
- (8) $A-S-CH_2-O-(CH_2)_a-SO_3-M$;

wherein M is chosen from a hydrogen atom and an alkali metal; X is chosen from a hydrogen atom, an alkyl group containing 1-10 carbon atoms, an aryl group, a linear or cyclic amino group containing 1-6 nitrogen atoms, 1-20 carbon atoms, and multiple hydrogen atoms, or a hetero cyclic group containing 1-2 sulfur atoms, 1-6 nitrogen atoms, 1-20 carbon atoms, and multiple hydrogen atoms; and a and b are independently an integer of 3-8.

- 3. The method of claim 1, wherein the compound comprising the formula -X-S-Y- is present in the electrolytic copper plating solution in the range of 0.1 100 mg/L.
- 4. The method of claim 1 wherein a concentration of a compound comprising a structure of $-X-S^-$ in the electrolytic copper plating solution is controlled in the range of 1.0 μ mol/L or lower.

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5. The method of claim 1 wherein the substrate is chosen from a printed circuit board and a wafer.

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- 6. The method of claim 1 wherein the substrate comprises through holes or via holes.
- 7. The method of claim 1 further comprising the steps of contacting the substrate with the electrolytic copper plating solution and applying sufficient current density to deposit copper on the substrate.
- 8. A method of treating an electrolytic copper plating solution comprising the step of contacting the electrolytic copper plating solution with ozone, wherein the electrolytic copper plating solution comprises a compound comprising the formula of –X-S-Y-, wherein X and Y are independently chosen from hydrogen atom, carbon atom, sulfur atom, nitrogen atom, and oxygen atom, and X and Y may be the same only when they are a carbon atom.